GRANULAR ACTIVATED CARBON AS A TOXICITY REDUCTION TECHNOLOGY FOR WASTEWATER TREATMENT

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Introduction

The Clean Water Act governs the discharge of wastewater to all navigable waterways in the U.S. It is the explicit purpose of this Act to prevent the discharge of "toxic pollutants in toxic amounts" to the nation's surface water supplies. To achieve this goal, the National Pollutant Discharge Elimination System (NPDES) was established, whereby a facility wishing to release wastewater to a surface water system must obtain a permit to do so. This NPDES permit contains the wastewater quality criteria that must be met before the wastewater can be legally discharged.

Historically, specific chemical limits have been used for establishing the quality of a wastewater discharged from a facility. The EPA developed a list of priority pollutants for which maximum discharge concentration limits were established. This regulatory approach had the advantage that straightforward protocols with clearly defined quantification limits were available for compliance and testing purposes. However, it became increasingly apparent that there were weaknesses with this approach when it was used exclusively. Many chemicals not included in the priority pollutant list will produce toxic responses from indigenous biota when released to a surface water. Therefore, the EPA developed methods for directly assessing the potential toxicity a discharge may generate in a receiving stream. The protocols and techniques for performing toxicity tests have been refined to the point the EPA is comfortable including them as another method for regulating the quality of a permitted discharge [1,2,3].

As a result, there is now increased attention on quantifying the toxicity, or potential toxicity, of wastewaters from industrial facilities and publicly owned treatment works (POTWs). Therefore, as these facilities renew their NPDES permits, toxicity testing and/or toxicity limits are being increasingly introduced. Since biological systems are often more sensitive to pollutants than can usually be quantified by conventional analytical methods, dischargers are faced with achieving more stringent water quality goals.

This paper will present several case studies to illustrate how certain facilities have used granular activated carbon (GAC) to achieve compliance with these more stringent regulations.

What Is Toxicity?

Toxicity is operationally defined as any adverse biological effect [4]. It is classified as either acute or chronic in nature. The adverse effect monitored for acute toxicity is organism death, while chronic toxicity can be any deviation from normal growth or behavior for an organism. Toxicity may be reported as a concentration (or the percent solution of wastewater mixed with a control water), as Toxicity Units, or as "% Survival." Tests for determining acute toxicity are usually shorter in duration than those for chronic toxicity. Acute tests are typically completed within 48 hrs, while chronic tests may last much longer (full chronic tests could last a year or more). Table 1 presents a comparison of acute and chronic testing. Dischargers that have acute tests in their current permits may have more sensitive species or chronic tests included when their permits are renewed. Chronic criteria are often more difficult to satisfy than acute criteria. Thus, the inclusion of a more sensitive specie or a chronic test means the discharger is again faced with a more stringent effluent quality requirement.

Resolving Toxicity Problems

A facility that expects to receive toxicity limits or toxicity test requirements may do preliminary testing to determine whether they will have a compliance problem. If the results indicate the presence of unacceptable levels of toxicity, a "Toxicity Reduction Evaluation" (TRE) must be completed to determine how to eliminate or reduce the toxicity to acceptable levels. A TRE can be very time consuming and costly, particularly if a complex wastewater is involved. Figure 1 presents a schematic of the steps involved in a TRE.

Included in the TRE is a systematic attempt to identify the chemical(s) causing the toxicity. This so-called "Toxicity Identification Evaluation" (TIE) can have one of three outcomes [5]; 1.) a specific chemical is identified, 2.) a particular wastewater fraction is consistently identified as toxic, or 3.) no specific chemical or fraction is consistently identified as causing the toxicity.

If (1) is the outcome, it is a straightforward matter to design treatment systems to remove specific contaminants. If (2) or (3) is the outcome, it becomes more difficult to choose an appropriate treatment technique and considerable effort will be required to prove the best alternative(s). However, if organics are implicated as a source of toxicity, activated carbon should be considered as a toxicity reduction technology.

To illustrate this point, several case studies will be reviewed below. These studies include three oil refineries and a chemical manufacturing facility. In some cases, studies were not optimally designed, while others were. Also, one of the examples is of a successful program that subsequently required optimization.

CASE STUDY 1 - REFINERY A

Refinery A treats a sour crude oil. It became apparent that toxicity testing using Daphnia would be included when they renewed their NPDES permit. Their treatment system consisted of pH adjustment and a equalization/bio-treatment pond and would not produce an effluent complying with the new permit. A series of toxicity reduction treatability studies were begun, rather than a systematic TRE, to determine what methods might remove the toxicity. The technologies tested as tertiary treatments to Activated Sludge (AS) processes were ClO_2, H_2O_2, O_3, and GAC. Table 2 presents the results of the batch tests completed with these technologies. The results indicated that AS and or Activated Sludge-Powdered Activated Carbon (AS-PAC) followed by ClO_2 or H_2O_2 actually increased their toxicity. However, tertiary treatment with O_3 or GAC reduced the effluent toxicity to satisfactory levels. Unfortunately, because a treatability-based toxicity reduction approach was used rather than an organized TRE which included a TIE, the presence of NH_3 excursions in the refinery caused inconsistent results in some aspects of the study. Thus, it was decided that an AS system with PAC addition could provide sufficient performance during the interim while sources of NH_3 were traced and reduced. The addition of GAC polish would be considered if operational experience showed that it was needed to ensure compliance. GAC was chosen over O_3 due to its cost effectiveness.

CASE STUDY 2 - REFINERY B

Refinery B processes heavy crudes. The wastewater treatment system consisted of API separators, DAF units, an aerated bio-pond and clarification pond. This refinery was informed that a sensitive toxicity test (a 96 hr flow through trout test) was going into their renewed permit. Due to the timing of the permit renewal, the refinery did not attempt to evaluate any toxicity reduction technologies. Instead, a survey of similar facilities with similar permits was made and GAC was found to be the preferred technology. Thus, while installation of a full scale GAC system proceeded, a pilot study was conducted to prove GAC worked and to determine the GAC use rate. Table 3 provides a description of the pilot system and Figure 2 presents the study results. A GAC use rate of 0.4 lb/1000 gal was determined in the pilot study for this refinery. Due to improved performance from their bio-treatment system over time, the full scale system has operated at an even lower use rate.

The refinery did not stop at this point. In anticipation of stricter limits in the future, a TIE is underway at the refinery to determine what the toxicants are and where they are generated. The plan now is to reduce the toxicity at the source an improve the GAC use rate further. An optimization of the GAC system may occur in the future, as a result.

CASE STUDY 3 - REFINERY C

Refinery C treats heavy crudes. The wastewater system included API separators, DAF units, coagulation and biological treatment. However, a polish operation was needed to achieve compliance with the refinery's acute toxicity limits for 3-spined stickleback. After some preliminary screening studies, GAC was chosen as the technology for achieving compliance and a custom system was successfully installed and operated for the life of the permit.

When the refinery renewed its permit, after five years of compliance, a more sensitive specie (trout) was required for toxicity testing. As a result, the refinery had to re-evaluate the current system for compliance with new criterium, >95% survival for a 96 hr flow through trout test. An optimization study was initiated to determine whether the system could be operated more economically while still satisfying the new permit. Table 4 provides the operating conditions for the tests and Figure 3 illustrates the results of this optimization study. Result for the full-scale system under normal operation are included in Figure 3. A change in the operation of the full scale system was recommended to satisfy the new permit and provide a more cost effective use rate. The carbon use rate could be reduced from >2.5 lb/1000 gal to 1.7 lbs/1000 gal.

CASE STUDY 4 - SPECIALTY CHEMICAL PLANT

A chemical plant had to meet toxicity limits for two species, Daphnia and fathead minnows. Its wastewater treatment system consisted of pH adjustment, activated sludge, and clarification. The expected toxicity limits were exceeded for both species. A thorough TRE was completed and several treatment technologies were evaluated for toxicity reduction, as a result. However, only GAC consistently reduced the toxicity to acceptable levels. An extensive pilot study was completed to determine optimal operating conditions and other design information for a GAC system. Table 5 presents a summary of the pilot test conditions that evaluated performance at 30 and 40 gpm. Figures 4 and 5 present results for tests completed at 30 gpm.

The use rate for the 30 gpm test averaged 3.02 lb/1000 gal and the use rate for the 40 gpm averaged 1.62 lb/1000 gal. The apparent discrepancy between these two use rates is reflected by two differences between the tests. First, the activated sludge plant did a much better job removing toxicants during the 40 gpm tests. Second, a sand filter for solids removal was included in the 40 gpm study, which reduced backwash frequency and removed some toxicity which was attributable to the solids in the wastewater.

It was of interest to note in these case studies that toxicity breakthrough could not be unequivocally correlated to any of the routine monitoring parameters used at the facilities. Also, toxicity breakthrough did not correlate with specific chemical breakthrough. Thus, one of the challenges in operating a GAC system for toxicity reduction is deciding upon a monitoring method to determine change out. With flow through toxicity tests, monitoring between GAC vessels in series can be done and change outs based on a certain percentage of toxicity breakthrough in a lead bed. In other cases, a global parameter such as TOC or COD may consistently achieve 100% breakthrough before toxicity breakthrough. In these cases, the global parameters may be useful monitoring tools. Some facilities have successfully based change outs strictly on a timed schedule.

Table 6 summarizes the use rate information for the studies reported here by providing an estimate of the cost for treating the specific wastes. Overall, these results were such that they provided attractive economics, compared to other technologies, for the facilities that have installed or will install GAC for toxicity reduction.

Summary

The case studies presented have served to illustrate that GAC provides an effective, yet flexible means for reducing the toxicity of wastewater where organics are a source for at least some of the toxicity. Compared to alternate technologies, GAC has been shown to be cost effective in achieving compliance goals. It also offers the opportunity for further optimization should GAC be installed to achieve one toxicity goal and another more stringent goal is introduced at a later date.

References

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TABLE 1
Comparison of Acute and Chronic Toxicity Tests

Acute Toxicity	Chronic Toxicity
Effect observed is organism death. Usually is a short term test (<96 hr).	Effect observed can be growth inhibition, reduced reproduction, behavioral changes, or other life cycle changes. Full chronic tests may last 30 days - 1 yr. EPA subchronic tests usually last 4-8 days.
Advantages Standardized protocols Relatively rapid and less expensive Endpoint easy to identify	Advantages More sensitive than acute tests Assess parameters other than death
Disadvantages Indicates only fatal concentrations Assumes fast acting toxicants May not reflect real world exposure	Disadvantages More costly and time intensive than acute End points more difficult to recognize More difficult protocols

TABLE 2
Results of Tertiary Treatment Technologies After AS for Refinery A

Treatment	Average % COD Removal	Effect on Toxicity Chronic	Acute
O_3	5.8	decreased	decreased
H_2O_2	-13.1	increased	increased
ClO_2	n/a	increased	increased
GAC	80.3	decreased	decreased

TABLE 3
Pilot Test Unit Description and Testing Conditions for Refinery B

Flow Velocity (gpm/ft^2)	4.2
Adsorber Diameter (ft)	4.0
Weight GAC/vessel (lbs)	2000
Average TOC (mg/l)	- (range 13-105)
Average COD (mg/l)	63
Average TSS (mg/l)	6 (range 2-45)

TABLE 4
Pilot Test Unit Description and Testing Conditions for Refinery C

Flow Velocity (gpm/ft^2)	5.4
Adsorber Diameter (ft)	0.125
Weight GAC/vessel (lbs)	0.45 (6 columns in series)
Average TOC (mg/l)	53
Average COD (mg/l)	162

TABLE 5
Pilot Test Unit Description and Testing Conditions for Chemical Plant A

Flow Velocity (gpm/ft^2)	2.39/3.18
Adsorber Diameter (ft)	4.0
Weight GAC/vessel (lbs)	2000
Average TC (mg/l)	95
Average TOC (mg/l)	48
Average TSS (mg/l)	25

TABLE 6
Treatment Costs for Toxicity Reduction Using GAC

Site	$/1000 gal
Refinery A	n/a
Refinery B	0.5
Refinery C	1.4
Chemical Plant A	1.4

Figure 1: Schematic of a systematic TRE.

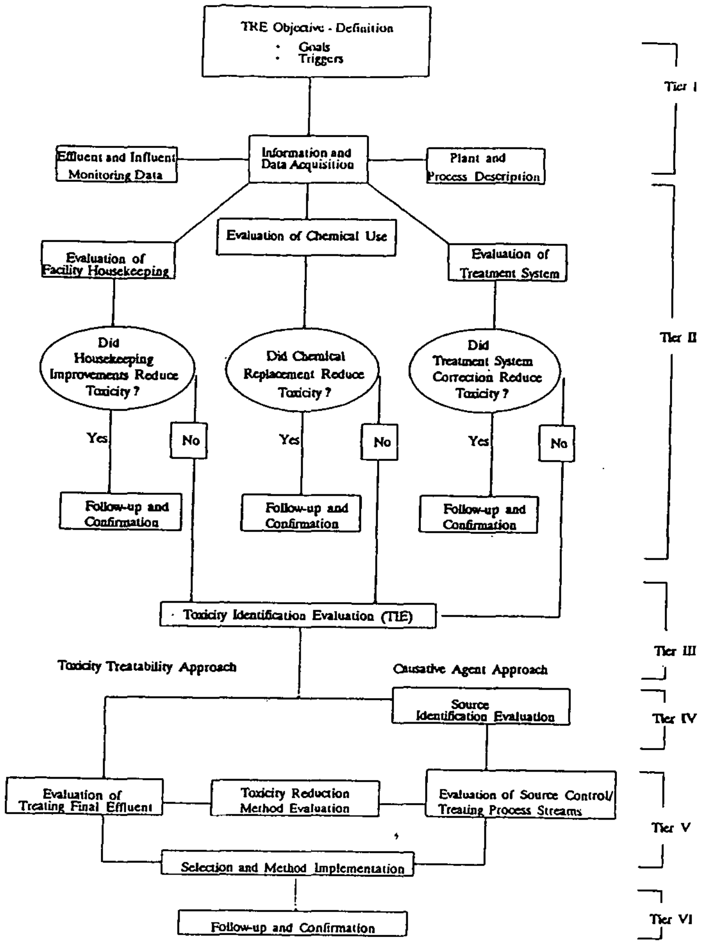

Figure 2: Toxicity data from the pilot study for Refinery B.

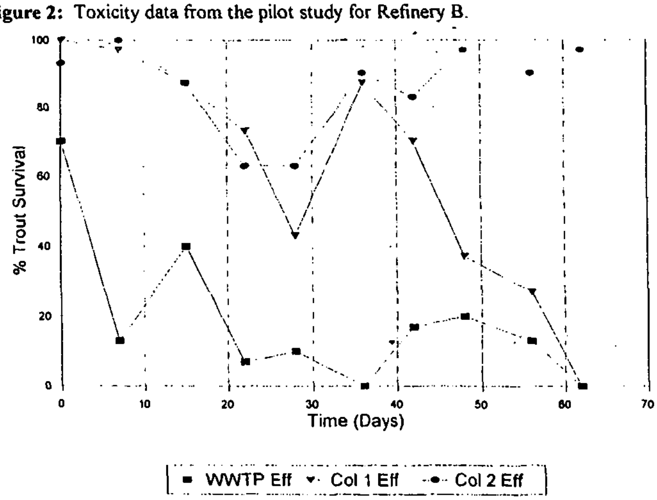

Figure 3: TOC breakthrough data with toxicity data superimposed for the Refinery C optimization study. Data for toxicity breakthrough from the commercial system is also included.

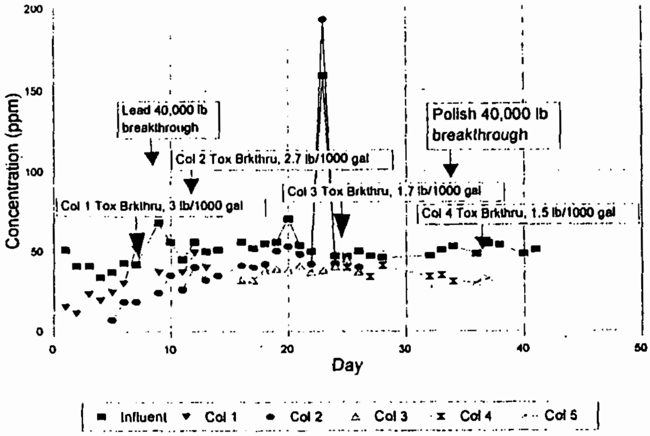

Figure 4: Daphnia toxicity data from the Chemical Plant A pilot study.

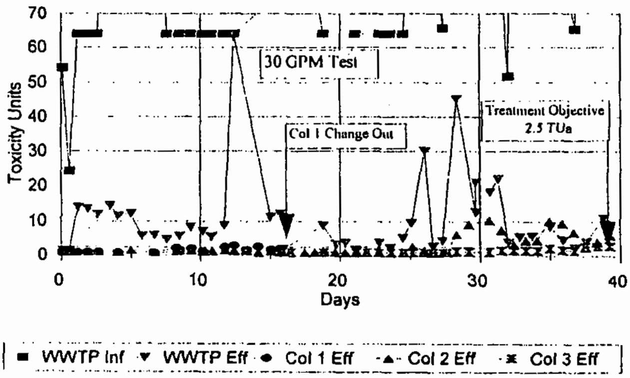

Figure 5: Fathead minnow toxicity data from the Chemical Plant A pilot study.